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Si_3N_4 and Si_3N_4/SiC composite rings for dynamic sealing of circulating fluids

J.M. Carrapichano [a], J.R. Gomes [b,*], F.J. Oliveira [c], R.F. Silva [c]

[a] *Department of Mechanical Engineering, Coimbra Superior Engineering Institute, 3040-228 Coimbra, Portugal*
[b] *Department of Mechanical Engineering, CIICS, University of Minho, 4800-058 Guimarães, Portugal*
[c] *Department of Ceramics Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

Abstract

Silicon nitride (Si_3N_4) and silicon nitride/silicon carbide (Si_3N_4/30 wt.% SiC) seal rings were tested as self-mated pairs and dissimilar sealing systems against grey cast iron. The tribological experiments were conducted in a ring-on-ring tribometer at $V \approx 4\,m\,s^{-1}$ of linear speed, in the range of 0.3–1 kN of applied load, under a pressure of 2×10^5 Pa of a mixture of 20 vol.% of hydrogen peroxide in deionised water, which gives an effective pressure (P) between 0.2 and 1.3 MPa. The homologous tribosystems are ineffective to seal due to catastrophic abrasive wear. The system with better performance is the dissimilar pair Si_3N_4/grey cast iron, that presented wear coefficient values of $K = 4.2 \times 10^{-8}\,mm^3\,N^{-1}\,m^{-1}$ for the ceramic ring and $K = 1.3 \times 10^{-7}\,mm^3\,N^{-1}\,m^{-1}$ for the metallic ring, in tests driven for about 60 h and 890 km, with full sealing. An amorphous passivating film of silica protects the ceramic surface. This system still presents an excellent combination $K \times PV \approx 0.1\,\mu m\,h^{-1}$, this product being a measure of the surface loss of a machine component for a given time of service.

Keywords: Mechanical seals; Tribology; Ceramics; Composites

1. Introduction

Mechanical seals protect the environment from product leakage in equipment with rotating shafts or alternative movement parts (i.e. pumps, agitators, automotive engines, compressors, turbines, etc.). Outflow control is crucial when the working fluids are toxic, corrosive, flammable or explosive. Ceramics are attractive candidates for this application due to their combination of high-temperature hardness, high contact fatigue resistance, corrosion resistance and low inertial mass. Among this class of materials, silicon carbide (SiC) and alumina (Al_2O_3) are already applied as mechanical rings [1,2]. However, low fracture toughness is their main disadvantage. Furthermore, a demanding technology is needed to fully densify SiC, as very high sintering temperatures are required, which makes this ceramic an expensive and laborious product.

In the present work, a prototype of a new system of ceramic mechanical seals based on silicon nitride (Si_3N_4) is proposed. Monolithic or SiC reinforced Si_3N_4 materials are compared. The sealing system is tribologically tested with a ring-on-ring configuration in an aggressive circulating fluid. Self-mated ceramic and ceramic/grey cast iron tribosystems are investigated. This approach, by using real components in working conditions, further advances the tribological testing of such materials already performed in common pin-on-ring apparatus [3–6].

2. Experimental details

The tribological experiments were performed in a microprocessor controlled rotary tribometer (TE-92 Plint & Partners) in ring-on-ring planar contact configuration, according to the ASTM D3702-94 standard, to simulate the sealing face operation. A sketch of the testing zone together with a picture of a ring pair is given in Fig. 1. The tests were conducted at room temperature, with constant rotational speed of $w = 2000$ rpm (linear speed, $V \approx 4\,m\,s^{-1}$), at a normal load (N) varying from 0.3 to 1 kN, under a pressure of 2×10^5 Pa of a mixture of 20 vol.% of hydrogen peroxide in deionised water. The effective pressure (P) on the contacting surfaces was between 0.2 and 1.3 MPa. The real time friction coefficient values (f) were appraised by a load cell, the average value taken from several steps (a minimum of four) within a total sliding distance between

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[*] Corresponding author. Tel.: +351-253-510232; fax: +351-253-516007.
E-mail address: jgomes@dem.uminho.pt (J.R. Gomes).

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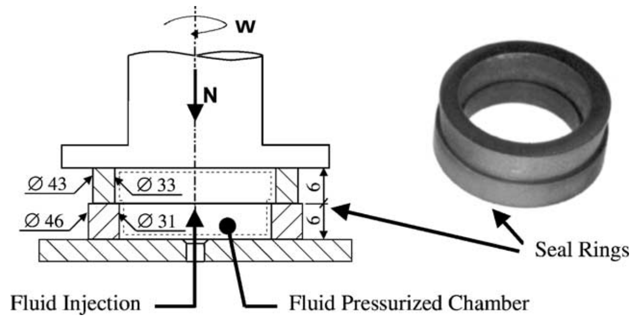

Fig. 1. Sketch of the geometry of the ring-on-ring tribological test under internal fluid pressure (w—rotation speed of the upper ring; N—normal applied load). Rotating sample—upper ring; fixed sample—lower ring.

66 and 890 km, depending on the wear resistance of the sliding pair. The wear coefficient (K) is the ratio between the volume loss, assessed by weighing the samples at the final of each step, and the product of the effective load by the sliding distance. Both friction and wear coefficients were calculated in steady-state condition where almost constant values are observed, after a well-defined running-in period characterised by rising tribological parameters.

Mechanical rings of two grades of ceramic materials, a monolithic Si_3N_4 and a Si_3N_4/30 wt.% SiC composite, were full densified by pressureless sintering (1750 °C, 120 min, N_2 atmospheric pressure) followed by planar grinding and polishing. The final dimensions of the upper and lower rings for the tribological testing (Fig. 1) are, respectively, 43 mm × 33 mm × 6 mm and 46 mm × 31 mm × 6 mm (external diameter × internal diameter × thickness). The compositions of the Si_3N_4 bulk grade and the Si_3N_4 matrix of the composite are the same: 89.3 wt.% Si_3N_4 (HC Starck M11)–3.7 wt.% Al_2O_3 (Alcoa 116SG)–7.0 wt.% Y_2O_3 (HC Starck C fine). The SiC reinforcement phase of the ceramic composite has a particulate geometry with average size of 0.8 μm (HC Starck A10). Vickers hardness and fracture toughness were determined with 98 N of indentation load giving the following values: 12.1 GPa and 6.0 MPa m$^{1/2}$ for the Si_3N_4 ceramic and 14.9 GPa and 6.2 MPa m$^{1/2}$ for the Si_3N_4/30 wt.% SiC composite. Grey cast iron (GCI) rings (3.9 wt.% C–2.9 wt.% Si–0.9 wt.% Mn; 1.9 GPa of hardness) were machined from commercial ingots. The initial roughness (R_a) values of the working faces were 0.067, 0.114 and 2.194 μm, respectively, for the Si_3N_4, Si_3N_4/30 wt.% SiC and the GCI materials. Morphological and chemical analysis of the worn surfaces of the rings was performed by SEM/EDS.

3. Results and discussion

Table 1 presents the friction and wear coefficients of the tested pairs together with the final surface roughness of the worn rings. The product of the effective pressure at the ring contact by the linear speed (PV) is a common useful parameter to assign the working range of a face seal system, the minimum value corresponding to the onset of sealing and the maximum value being related to a suitable lifetime. The present PV values in Table 1 match the former criteria in the case of the dissimilar pairs. The tribological behaviour of the homologous contact Si_3N_4/Si_3N_4 for a similar PV condition is also presented, although this system did not attain a sealing condition due to early surface damage. A complementary study to the present one in a wide PV range (0.005–5.16 MPa m s^{-1}) confirmed the inadequacy of this pair for mechanical sealing of the tested fluid [7].

The morphology of the Si_3N_4 worn surfaces of the ceramic rings in self-mated contact is depicted in Fig. 2a–d. Under $P = 0.2$ MPa ($N = 0.3$ kN), the system ran with slight vibration although presenting some leakage. The fluid did not flow uniformly between the rings, resulting in the instantaneous absence of lubricant in some regions. A polished appearance is evidenced in the overall view of the Si_3N_4 surface for the case of the Si_3N_4/Si_3N_4 experiment (Fig. 2a). However, the higher magnification in Fig. 2b denotes the existence of abrasive grooves and grain pullouts, which is corroborated by the roughness value in Table 1 that is eight times higher than the initial value. Furthermore, EDS analysis revealed that the surface is fully covered by a silica rich film, the atomic oxygen percentage increasing to 29% in comparison with a nominal content of 5%. This is a consequence of a tribochemical action under the aqueous media [8]. This tribolayer protected the ceramic in the given test conditions, resulting in the relatively low wear coefficient for the Si_3N_4/Si_3N_4 contact in Table 1. In order to achieve an efficient sealing, the applied load on the rings was increased up to 1 kN but the system responded with unacceptable mechanical vibration. The morphology of the contact surfaces in Fig. 2c and d at this load gives evidence of large surface damage by fracture. This wear mode is a

Table 1
PV product (P—effective pressure; V—linear speed), friction (f) and wear (K) coefficients, and final roughness (R_a) values for the distinct ring-on-ring tested pairs

Tested pair	PV (MPa m s^{-1})	f	K (mm^3 N^{-1} m^{-1})		R_a (μm)	
			Upper ring	Lower ring	Upper ring	Lower ring
Si_3N_4/Si_3N_4	0.86	0.12	6.7×10^{-8}	6.7×10^{-8}	0.448	0.306
Si_3N_4/GCI	0.70	0.15	4.2×10^{-8}	1.3×10^{-7}	0.082	1.258
Si_3N_4/30 wt.% SiC/GCI	0.62	0.15	5.9×10^{-6}	5.3×10^{-7}	0.132	2.000

Si_3N_4—silicon nitride; GCI—grey cast iron.

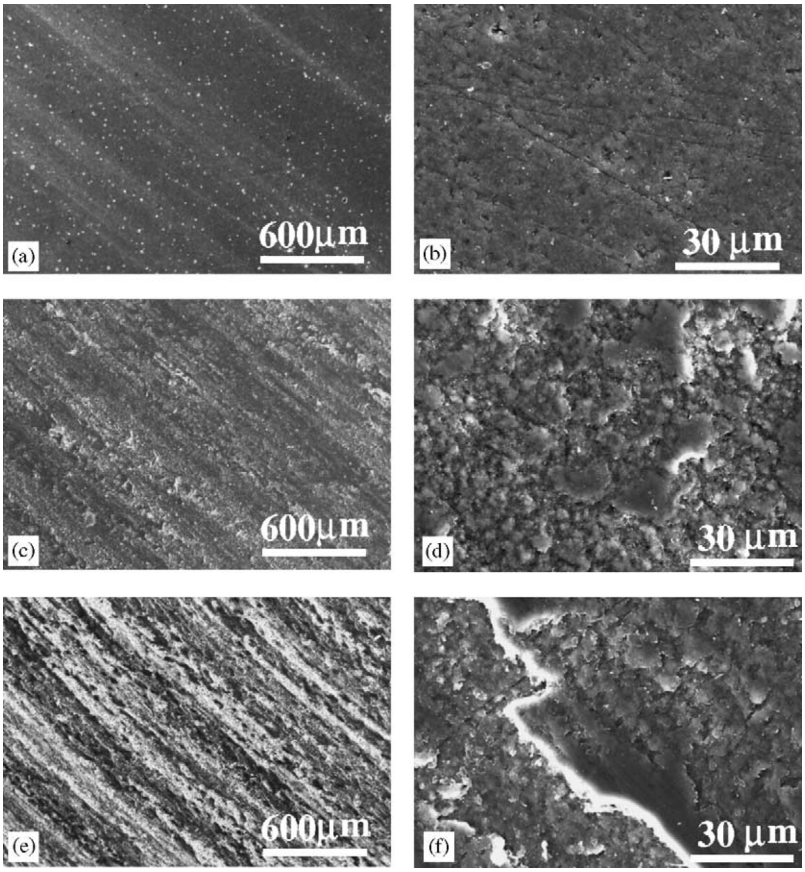

Fig. 2. SEM micrographs of ceramic worn surfaces corresponding to the self-mated pairs with Si_3N_4 (a–d) and Si_3N_4/30 wt.% SiC composite (e and f). The applied load is 0.3 kN (a and b) and 1 kN (c–f).

direct consequence of the brittle response of the ceramic at the transient dry contact sites, whenever the critical failure load is attained. The worn surfaces present alternating regions of fractured exposed material and covered tracks with aggregated wear debris that were plastically deformed along the sliding direction. This behaviour was extensively analysed in a prior work using pin-on-disc experiments [5].

A similar tribological response was observed for the homologous pairs of Si_3N_4/SiC composite, although with the previously observed severe wear regime operating even at low loads. Fig. 2e and f reveal extensive surface destruction by fracture that was even worse than in monolithic material. The same happened in pin-on-disc test configuration, which was explained by the lack of mechanical resistance of the weak dispersoid/matrix interface, leading to easy SiC debonding and particle pull-out [4].

The only effective mechanical seals were those based on the dissimilar ceramic/metal combination. The respective values of the friction and wear coefficients in full sealing conditions (second and third rows in Table 1) denote the superior behaviour of the monolithic material that present a moderate wear coefficient in the order of magnitude of $10^{-8}\,mm^3\,N^{-1}\,m^{-1}$. For comparison, a friction coefficient value of 0.07 and a wear coefficient of $K = 10^{-6}\,mm^3\,N^{-1}\,m^{-1}$ is reported for a common mechanical seal system consisted of graphite carbon/grey cast iron pair [9,10]. The $K \times PV$ product for the ceramic component in this tribopair is approximately $0.1\,\mu m\,h^{-1}$, this parameter being a measure the surface loss of a machine component for a given time of service.

The surface roughness values after testing (Table 1) were very close to the initial values (0.067 μm for Si_3N_4 and 0.114 μm for Si_3N_4/SiC) meaning that a high polishing level was kept. In accordance to this, the worn Si_3N_4 surfaces are very smooth, as depicted in Fig. 3a and b, respectively, of the final morphologies near the outer and the inner ring contact areas. An oxidised layer as proved by EDS analysis covers both zones, although the tribolayer is thinner in the former zone than in the later (17 and 24 at.% O, respectively, comparatively to 5 at.% O of nominal value). The inner contact area has a facilitated access to the fluid (Fig. 1) thus the reaction between the ceramic material and the aqueous media is improved and the tribofilm is thickened. The mating grey cast iron surface at the inner zone has a similar morphology (Fig. 3d), the metal being covered by an extensive oxidised layer. The film crack pattern on both the ceramic (Fig. 3b) and the metal (Fig. 3d) surfaces indicates that it has an amorphous, brittle, nature. The oxide protection of the metal alloy

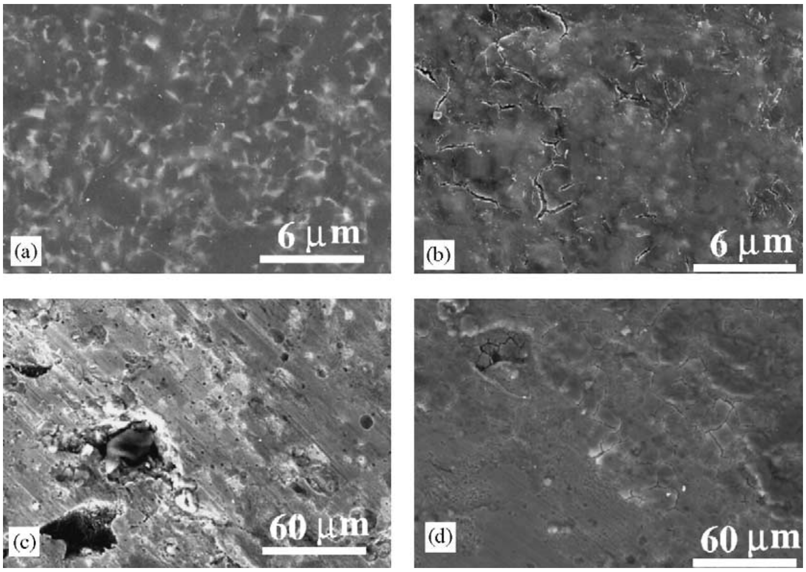

Fig. 3. SEM micrographs of the Si_3N_4 (a and b) and grey cast iron (c and d) ring surfaces after sliding against each other. (a and c) Outer areas of the rings; (b and d) inner zones.

is not so effective at the outer area, where a few graphite flake cavities remain exposed (Fig. 3c). The combination of amorphous or crystalline silica, graphite and Fe_2O_3 in the tribofilm that develops at the Si_3N_4/grey cast iron contact under distilled water lubrication is reported to offer good tribological properties [11], as in the present study. The values of the final surface roughness of GCI in Table 1 show a slight improvement compared to the initial value of 2.194 μm.

Similarly to the above-described self-mated pairs, the addition of SiC particles to the Si_3N_4 matrix has a detrimental effect on the wear resistance, the wear coefficient increased two orders of magnitude. Also, the worse mechanical characteristics of the Si_3N_4/SiC composite resulted in a poorer tribological response of the GCI opponent ring, as shown by the highest wear coefficient value obtained (Table 1).

4. Conclusions

Ceramic rings made of Si_3N_4 and Si_3N_4/30 wt.% SiC composites were tested for mechanical seals application. As self-mated systems, they do not provide efficient sealing to a mixture of 20 vol.% of hydrogen peroxide in deionised water, in common *PV* conditions (effective pressure, *P*, between 0.2 and 1.3 MPa; linear speed, $V \approx 4\,\mathrm{m\,s^{-1}}$). At the lowest pressure, the ceramic surfaces are protected from wear by a silica film resulting from the tribochemical action of the strong oxidising media, although some fluid leakage occurs. If the applied load between the rings is increased, the ceramic surfaces are severely damaged by a fracture wear mode as a consequence of their brittle nature, this behaviour being worse on the ceramic composite characterised by weak dispersoid/matrix interfaces.

An opposite result is obtained when a Si_3N_4 ceramic-based ring is combined with a grey cast iron antagonist ring. With this mechanical seal system, fluid leakage is completely avoided, the ceramic material presenting a moderate wear coefficient (*K*) in the range of $10^{-8}\,\mathrm{mm^3\,N^{-1}\,m^{-1}}$. The ceramic/grey cast iron contact is protected by a tribolayer composed of amorphous silica and ferrous oxide. In a sliding distance of 890 km, the surface loss is estimated to be approximately $0.1\,\mu\mathrm{m\,h^{-1}}$, as given by the product $K \times PV$.

Acknowledgements

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References

[1] R. Divakar, in: S. Jahanmir (Ed.), Friction and Wear of Ceramics, Marcel Dekker, New York, 1997, pp. 357–381.
[2] M. Brown, Seals and Sealing Handbook, Elsevier, Amsterdam, 1995.
[3] J.R. Gomes, A.S. Miranda, R.F. Silva, J.M. Vieira, Mater. Sci. Eng. A 209 (1996) 277–286.
[4] J.R. Gomes, M.I. Osendi, P. Miranzo, F.J. Oliveira, R.F. Silva, Wear 233–235 (1999) 222–228.
[5] J.R. Gomes, F.J. Oliveira, R.F. Silva, M.I. Osendi, P. Miranzo, Wear 239 (2000) 59–68.
[6] A. Skopp, M. Woydt, K.H. Habig, Wear 181–183 (1995) 571–580.
[7] J.M. Carrapichano, Comportamento Tribológico de Anéis Vedantes Compósitos de Nitreto/Carboneto de Silício, Ph.D. Thesis, University of Aveiro, Portugal, 2002.
[8] K. Kato, in: Proceedings of the Second World Tribology Congress, Vienna, Austria, 3–7 September 2001 (CD-ROM).
[9] http://www.johncrane.com/technical/ (accessed in June 2001).
[10] R. Johnson, K. Schoenherr, in: M.B. Peterson, W.O. Winer (Eds.), Wear Control Handbook, ASME, 1980, pp. 727–753.
[11] Y. Gao, L. Fang, J. Su, Z. Xie, Wear 206 (1997) 87–93.